

PATENT SPECIFICATION

- NO DRAWINGS

902,590



Date of Application and filing Complete Specification March 9, 1961.

No. 8744/61.

Application made in United States of America (No. 16632) on March 22, 1960.

Complete Specification Published Aug. 1, 1962.

Index at acceptance:—Class 2(3), C1C(1B:7A:11B).

International Classification:—C07c.

COMPLETE SPECIFICATION

Production of Heptafluoropropane

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of 1,1,1,2,3,3,3-heptafluoropropane, $\text{CF}_3\text{CFHCF}_3$, b.p. -17 to -18.5°C . (hereinafter referred to simply as heptafluoropropane) by direct hydrofluorination of hexafluoropropene, $\text{CF}_3\text{CF}=\text{CF}_2$, b.p. -29°C . Heptafluoropropane is useful as a propellant and as a gaseous dielectric.

It has been proposed to make heptafluoropropane by a procedure involving liquid-phase reaction between hexafluoropropene and aqueous hydrofluoric acid in a pressure vessel at substantial superatmospheric pressures. The disadvantages of batch, liquid-phase, autoclave operations are apparent.

It has now been found that activated carbon by itself possesses the power of promoting reaction of anhydrous hydrogen fluoride and hexafluoropropene in an easily controllable, all gas-phase, catalytic process in which heptafluoropropane is made in high yields. It is also of major importance, from the standpoint of simple operation, that activated carbon promotes the reaction at substantially atmospheric pressure, and requires only moderately elevated reaction temperatures.

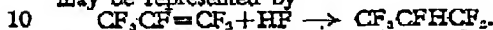
Generally, the practice of the invention includes effecting reaction between gaseous hexafluoropropene and gaseous substantially anhydrous hydrogen fluoride at moderately elevated reaction temperatures and substantially atmospheric pressure and in the presence of activated carbon at catalyst, and recovering heptafluoropropane from the resulting reaction products. More particu-

larly, gaseous hexafluoropropene and gaseous anhydrous hydrogen fluoride may be continuously metered, mixed and fed at substantially atmospheric pressure into a tubular reactor which is packed preferably full with activated carbon catalyst and which may be made of inert material such as nickel, "Monel", or "Inconel" or of steel lined with graphite or "Alundum", (the words "Monel", "Inconel" and "Alundum" being Registered Trade Marks), and enveloped in a suitable tubular electric furnace provided with automatic heating means to provide the reaction temperature. Product recovery may be effected by means generally conventional in this art. For example, vapours leaving the reaction zone may be passed through a water scrubber to remove hydrogen fluoride, and those leaving the scrubber may be dried and then totally condensed in the receiver by suitable cooling, such as by use of a Dry Ice-acetone mixture. The resulting condensate then may be fractionally distilled to facilitate recovery of the sought-for product, and separation of possibly small amounts of unreacted starting material which may be recycled if desired.

The activated carbon catalysts which are used in the practice of the invention may be granular materials which are readily available from several commercial sources, suitable materials being various grades of around 8-14 mesh activated carbon such as Columbia 6G, Columbia SW, and Darco. (The word "Darco" is a Registered Trade Mark.) The grain size is not highly critical. Ordinarily, the reaction is carried out in elongated tubular reactors, and it is then desirable to employ activated carbon granules of average mesh size between 1/20th and 1/4th of the reactor diameter; preferably the reactor is substantially completely filled with granules of average mesh size of about 1/8th or 1/10th of its diameter.

In order to secure the unusually high yields

obtainable by the practice of the invention, it has been found that the reaction zone temperature should be held in the range of 250—450° C. Experience indicates that the best yields appear to be dependent upon a correlation of temperature and mol ratio of hydrogen fluoride to hexafluoropropene starting material. The reaction involved may be represented by



Generally, the quantity of hydrogen fluoride used relative to hexafluoropropene starting material may be any amount sufficient to react with a substantial quantity of the hexafluoropropene, and if hexafluoropropene conversion and utilization of hydrogen fluoride per pass are not of major importance, hydrogen fluoride in amount less than theoretical may be employed. However, for better overall operation, the mol ratio of hydrogen fluoride to hexafluoropropene preferably should be in the range of 1:1 to 3:1. When high yields are desired, it is preferred to employ the hydrogen fluoride in amount in excess of the theoretical requirement, and for best yields (of or approaching 100% on the basis of the organic starting material fed) a mol ratio of hydrogen fluoride to hexafluoropropene in the range of 1.5:1 to 3:1 is preferred. As demonstrated in the appended examples, when utilizing hydrogen fluoride and organic starting material in the preferred mol ratio range, and employing reaction zone temperatures in the range of 375—425° C., substantially 100% yields of heptafluoropropane may be obtained.

A major advantage of the invention is that the reaction may be carried out efficiently at substantially atmospheric pressure as distinguished from the superatmospheric pressures characteristic of the prior art. It will be understood that in the practice of gas-phase catalytic processes of the general type described herein, i.e. processes in which a gas stream is caused to flow successively through reaction and product recovery systems, the pressure is considered for practical purposes as being substantially atmospheric even though it is sufficiently high on the input side to effect commercially satisfactory gas flow through the apparatus train. Thus, strictly speaking, depending upon factors such as apparatus design, mesh size of catalyst, unpacked gas space in the reactor, desired contact time, etc., the actual pressures in systems of the kind under consideration may vary from 2 up to say 10—15 pounds gauge, and accordingly operations of this type are regarded as being effected under substantially atmospheric pressure.

Contact time may be varied considerably without noticeable falling off in process efficiency. Generally, an increase in the contact time and reactor temperature results in higher utilization of the hydrogen fluoride

and conversion of hexafluoropropene, and a decrease in contact time and reactor temperature results in lower utilization of hydrogen fluoride and lower conversion. Contact times may lie in the range of 0.5—60 seconds, but will usually and preferably be in the range of 1—25 seconds. To a substantial extent, contact time, reactor temperature and ratio of reactants are inter-related, and depending upon the apparatus and the particular operation at hand, optimum conditions as to contact time may be determined by test runs.

In Examples I and II which follow, the reactor consisted of a 1 inch internal diameter nickel tube 42 inches long heated externally by an electric furnace enveloping about 30 inches of its length. The reactor was provided at the inlet end with suitable means for metered introduction of gaseous hexafluoropropene and anhydrous hydrogen fluoride, while the reactor outlet was connected to the inlet end of a products recovery train. The catalyst employed consisted of activated carbon (commercially available Columbia 6G grade) of 8—14 mesh, the size being such as to provide granules averaging about 1/10th of the reactor diameter. The reactor was completely filled with catalyst, the total volume amounting to about 0.54 litre. The pressure in the reactor system was about 3 lb. psig., i.e. sufficient to move the gas stream through the reactor system at the contact times indicated and through the remainder of the apparatus train. Percentages are by weight.

EXAMPLE I

During a period of about 125 minutes, about 77 grams (3.85 mols) of anhydrous hydrogen fluoride and about 308 g. (2.05 mols) of hexafluoropropene were premixed and metered into the reactor system. Throughout the run the temperature within the reactor was maintained in the range 392 to 402° C. Overall contact time was approximately 9 seconds. The vapours leaving the reactor were water-scrubbed to remove some hydrogen fluoride, dried by passage through a calcium chloride drying tower, and condensed and collected in a receiver cooled with Dry Ice-acetone. A total of 36.1 g. (1.81 mols) hydrogen fluoride was scrubbed out of the reactor exit gas. A total of 342 g. of material was condensed and recovered in the receiver. On distillation of the condensate, there were recovered 316 g. of material boiling in the range —16 to —17.5° C. and 25 g. of still residue. Analysis, including infra-red absorption spectrum analysis and gas chromatography, established both distillate and residue, a total of 341 g. (2.0 mols), to be heptafluoropropane. Hence, the yield on the basis of hexafluoropropene fed was substantially 100%.

902,590

3

EXAMPLE II

During a period of about 120 minutes 88 g. (4.40 mols) of anhydrous hydrogen fluoride and about 278 g. (1.85 mols) of hexafluoropropene were premixed and metered into the reactor. Throughout the run the temperature in the reactor was maintained in the range 300 to 306° C. Overall contact time was approximately 8 seconds. The vapours leaving the reactor were handled as in Example I. A total of about 43 g. (2.15 mols) of hydrogen fluoride was scrubbed out of the reactor exit gas, and a total of 316 g. of condensate was recovered in the Dry Ice trap. On distillation there were recovered as condensate about 291 g. of material boiling substantially in the range of -16 to -17.5° C. and 25 g. of still residuc. Analysis, including infra-red absorption spectrum analysis and gas chromatography, showed both distillate and residue to be heptafluoropropane, in total amount of 316 g. (1.86 mols). The yield based on hexafluoropropene fed was substantially 100%.

WHAT WE CLAIM IS:—

1. Process for the production of 1,1,1,2,3,3,3-heptafluoropropane, which comprises bringing a mixture of hexafluoropropene and substantially anhydrous hydrogen fluoride in the gas phase into contact with an active

carbon catalyst at a temperature of 250°—450° C.

2. Process according to Claim 1, wherein the reaction is effected under substantially atmospheric pressure.

3. Process according to Claim 1 or 2, wherein the mol ratio of the hydrogen fluoride to the hexafluoropropene is between 1:1 and 3:1.

4. Process according to Claim 3, wherein the mol ratio is between 1.5:1 and 3:1 and the reaction temperature is 375°—425° C.

5. Process according to any one of the preceding claims, wherein the mixture of hydrogen fluoride and hexafluoropropene is fed continuously into and through a tubular reaction zone containing the active carbon and heated to the reaction temperature, and the vapours leaving the zone are continuously treated to isolate heptafluoropropane therefrom.

6. Process for the production of 1,1,1,2,3,3,3-heptafluoropropane according to Claim 1, substantially as hereinbefore described.

7. 1,1,1,2,3,3,3-heptafluoropropane obtained by a process claimed in any one of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square, Gray's Inn,
London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained